



Study on titanium foil coated with partial reduction titanium dioxide as bipolar lead-acid battery's substrate



Xiaoshi Lang, Dianlong Wang^{*}, Shenzhi Tang, Junsheng Zhu, Chenfeng Guo

School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, PR China

HIGHLIGHTS

- A lay of TiO_{2-x} was coated on the Ti plate surface by sol–gel method.
- The properties of Ti foil's surface is the most excellent at 800 °C.
- Electrochemical performances of battery with $\text{Ti}/\text{TiO}_{2-x}$ as substrate are superior.
- In the cell cycle, the properties of $\text{Ti}/\text{TiO}_{2-x}$ as substrate can maintain stability.

ARTICLE INFO

Article history:

Received 15 March 2014

Received in revised form

22 July 2014

Accepted 2 August 2014

Available online 10 August 2014

Keywords:

Bipolar lead-acid battery

Substrate

Titanium foil

Partial reduction titanium dioxide

Sol–gel

Carbon thermal reduction

ABSTRACT

Pure titanium foil cannot be directly as the substrate for the bipolar lead-acid battery due to its surface oxidized into titanium dioxide in the cell cycle. The poor electronic conductivity of titanium dioxide will increase substrate's ohmic resistance and can affect the cell's electrochemical performances. In this paper, titanium foil's surface is coated with a lay of partial reduction titanium dioxide (TiO_{2-x}) which has excellent chemical stability and high electronic conductivity by means of sol–gel method. Through XRD, SEM and four-probe test, it shows that the modified titanium's surface has the most superior crystal structure and morphology and the highest electronic conductivity in the sintering temperature of 800 °C. We subsequently assemble bipolar lead-acid batteries with Ti coated by TiO_{2-x} as the substrate material. The batteries are discovered that when charged and discharged in 3.5 V–4.84 V at 0.5C the voltage between the charge and discharge voltage platform is 0.3 V, and the initial discharge specific capacity can reach 80 mAh g^{−1}. When the current rate is up to 1C and 2C, the initial discharge specific capacity is 70 mAh g^{−1} and 60 mAh g^{−1}. After 100 cycles, the initial specific capacity only decreases 12.5%.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The increasing concern for environmental pollution problems and the lack of petroleum resources makes the whole world start to find a suitable method to deal with these problems. At present, people find that consuming petroleum resources and polluting environment are mainly originated from the development of the automobile industry. So it is expected that development of hybrid electric vehicles (HEV) or electric vehicles (EV) will provide an opportunity to improve the situation. In the operation of the HEV and EV, the battery is the essential element to determine its cost, using range and performance and so it has become the focus of the

research. So far, various types of batteries can be as the power system for HEV and EV. It includes the lead-acid battery, Ni–MH battery, lithium ion battery, fuel cell and so on. Lead-acid battery is a type of the ideal power source for hybrid electric vehicles due to its simple structure, ripest craft, non-expensive technology, safety, and ease of recycling [1,2]. Nevertheless, batteries for HEV need the higher specific power and specific energy and longer cycle life, however, traditional lead-acid battery can't meet these requirements. Therefore, we need find a kind of novel pattern lead-acid battery to replace it.

Bipolar lead-acid battery is a type of promising lead-acid battery system. It has turned into the lead-acid battery's internal structure. Inside the bipolar lead-acid battery, there are some bipolar plates which are the positive (lead dioxide) and negative (lead metal) active materials respectively placed on both sides of a metal substrate. The number of bipolar plates decides the battery's work

^{*} Corresponding author.

E-mail address: wangdianlonghit@163.com (D. Wang).

voltage. And from the battery's structure, we can know that the more bipolar plates, the higher battery voltage. The schematic diagram of the bipolar lead-acid battery is presented in Fig. 1. The electrochemical mechanism of bipolar lead-acid battery is similar to traditional lead-acid battery, thus it has all lead-acid battery's advantage. From Fig. 1 we can see that in the charge and discharge process, the current vertically flows through the substrate from one cell to another. The current transfer mode can effectively shorten the current transmission path in order to reduce the ohmic resistance inside the battery and the current can be uniformly distributed on the surface of the substrate to decrease the active material's electrochemical impedance. Thus, the bipolar lead acid battery has the higher specific capacity and specific power and it can respond to the requirements of hybrid electric vehicles [3].

In the bipolar lead-acid battery, the substrate material is the most important part. It needs lightweight, corrosion resistance and high electronic conductivity. In the present reports, lead–tin alloy, ceramic, barium metaplumbate (BaPbO_3) and Ebonex[®] [4–6] were explored as substrate material for bipolar lead-acid battery. They were all ideal substrate material and some have previously started industrialization. Titanium foil is also an ideal substrate material due to its lightweight, high strength and corrosion resistance. From the bipolar plate structure, we can know that one side of the substrate for bipolar lead-acid battery is used as anode carrier and the other side as the cathode carrier. However, pure titanium foil as anode carrier is unreliable because its surface will be oxidized into a layer of titanium dioxide due to the positive high potential and strong oxidizing. This layer of titanium dioxide's low electronic conductivity will make the substrate of the bipolar lead no longer in force and the battery performance will be impacted seriously. Thus, the surface of titanium foils as substrate for bipolar lead-acid battery is expected to be modified.

Partial reduction titanium dioxide (TiO_{2-x}) is a kind of oxygen defective compound. There are limited oxygen vacancies in the titanium dioxide lattice. These oxygen vacancies can supply some channels for the electron conduction and so that, the electronic conductivity is more superior to titanium dioxide. In addition to the high electronic conductivity, this type of material also has outstanding chemical stability and binding with Ti foil very well. It can still keep stability in aggressive acid, alkali and oxidizing conditions [7]. At present, the synthesis method of TiO_{2-x} is just by means of reducing TiO_2 with hydrogen or carbon [8–10] at elevated temperature. Therefore, coating TiO_{2-x} on the Ti surface firstly needs to coat a layer of TiO_2 on its surface and then reduces it at the elevated temperature. Currently, major methods for coating TiO_2 on the Ti surface include chemical oxidation method [11], anodic oxidation method [12,13] and sol–gel method [14,15].

In this paper, we firstly coated a layer of TiO_2 with carbon source on the titanium foil surface using sol–gel method and then sintered

it at the elevated temperature in high purity argon atmosphere. Influences of titanium surface at different sintering temperatures were characterized through XRD, SEM and four-probe test. Subsequently, electrochemical performances of positive active material of bipolar lead-acid battery with modified titanium foil as substrate were also described by means of the charge and discharge test.

2. Experimental

2.1. Pretreatment of titanium foil

Before modifying titanium foil, it needs to be pretreated in order to improve its combination. 0.2 mm thickness of titanium foils were selected as the matrix. Firstly, they were soaked in saturated NaCO_3 solution at 60–70 °C to remove the surface grease. Secondly, they were mechanically polished with different abrasive papers, and washed clearly in an ultrasonic bath containing cold distilled water. Thirdly, chemically etched by immersion in $\text{HF}:\text{HNO}_3:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:2:3:12 in volume) mixed solutions to remove the surface oxide. Lastly, washed in distilled water and dried in air completely at room temperature.

2.2. Coated with TiO_{2-x}

Before sintering the titanium foil, the surface need to coat with a layer of TiO_2/C with sol–gel method. The method was similar to preparing Ti/TiO_2 electrode [14]. However, the difference is the fact that it requires adding some carbon source as the reducing agent. The precursor solution for Ti coated with TiO_2/C was established by the following way. 1.7 mL of tetrabutylorthotitanate and 0.2 mL of hydrochloric acid (37 wt%), which prevent the precipitation of oxides and stabilize the solutions, were dissolved in 6.8 mL of ethanol. After stirring for 30 min at room temperature, a mixed solution of 1.0507 g of citric acid and 6.8 mL of ethanol was tardily added to the above solution with a burette under stirring vigorously. After the mixture was agitated for 30 min, a clear sol was formed. Finally, 1 g of polyethylene glycol (PEG-2000) was in addition to the above solution to reduce its surface tension. And then, the solution was kept standing to perform hydrolysis reaction for 10 h that can lead to the formation of TiO_2 sol. In the process of hydrolysis reaction, the temperature should be between 25 °C and 35 °C. Too high temperature would destroy the stability of the TiO_2 sol, while too low temperature would make polyethylene glycol precipitated from the solution. Put the pretreated titanium foils into the TiO_2 sol solution for 30 s and then taken out in the air and dried the titanium foils at 80 °C for 1 h in order to remove organic components. After that the surface of the titanium foils was coated with TiO_2/C . At last the titanium foils were sintered at 600, 700, and 800 °C in high purity argon atmosphere for 2 h.

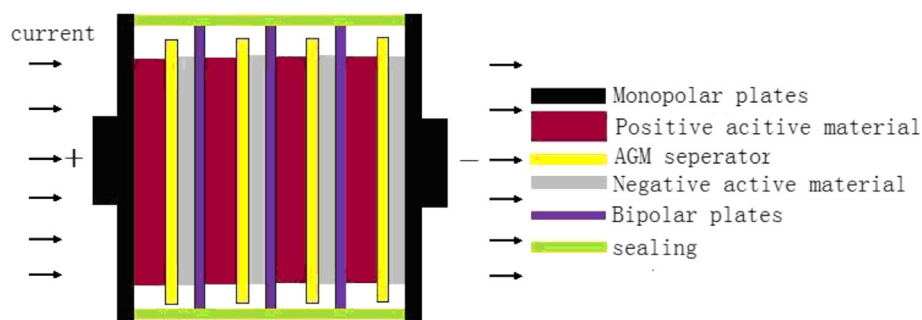


Fig. 1. The schematic diagram of the bipolar lead-acid battery.

2.3. Assembly of bipolar lead-acid battery

2.3.1. Paste preparation

Negative and positive pastes were prepared according to the conventional manner. Raw materials of positive paste were lead powder, red lead (Pb_3O_4), graphite, polypropylene fiber and SnSO_4 , and the raw materials of negative paste were lead powder, barium sulfate, lignosulphonate and humic acid. Firstly the raw material of the positive and negative pastes were mixed in a plastic container for 10 min. Distilled water was added to above mixture and mixed for 15 min. And then, sulfuric acid (1.4 g cm^{-3}) was slowly added. In the process of adding sulfuric acid, the lead paste is required to hold the temperature lower than 60°C with a water cooling system. At last, lead paste was mixed for a time period so that water, sulfuric acid and lead paste can be mixed adequately.

2.3.2. Electrode manufacturing and battery assembling

Firstly, after preparation of positive and negative pastes, one side of the modified titanium foils was pasted by negative and positive paste respectively as terminating anode and terminating cathode electrode. And on the same substrate one side pasted by negative paste and the other side pasted by positive paste was as a bipolar electrode. The thickness of coating negative and positive paste was 1 mm. And then, the pasted electrodes (terminating and bipolar electrodes) were cured in constant temperature and humidity instrument. Finally, cured plates as terminating and bipolar electrodes, absorptive glass mat (AGM) as separator and 1.26 g cm^{-3} sulfuric acid as electrolyte were used in the assembling of bipolar lead-acid batteries. The design and construction of the experimental battery are the same as the design of Keith Ellis et al. [6]. A 4 V experimental bipolar lead acid battery is illustrated in Fig 2. Before testing the battery, it required an internal formation process.

2.4. The investigations of modified titanium foil and bipolar lead-acid battery's electrochemical performances

In this paper, the characterization of titanium foils coated with TiO_{2-x} was using X-ray diffraction (XRD), scanning electron microscopy (SEM) and electronic conductivity test. XRD analysis was performed with a D Max-RD12Kw diffractometer with $\text{Cu K}\alpha$ radiation. The scan data were collected in the 2θ rang 10° – 90° at scan rate 2°min^{-1} . SEM was performed utilizing a Quanta 200 instruments. The electronic conductivity was tested by four-probe conductivity tester. The testing range of the instrument was 10^{-6} – $10^6 \Omega$.



Fig. 2. 4 V experimental bipolar lead acid battery.

Bipolar lead-acid batteries with modified titanium as substrate were tested galvanostatically between 3.50 and 4.84 V on multi-channel battery testers (Netware, Shenzhen in China) at 0.5C, 1C and 2C charge/discharge rates at room temperature. The current densities were calculated in accordance with Peukert equation. The specific capacities were determined on the basis of the weight of positive active material after curing.

3. Results and discussion

3.1. Characterization of the modified titanium foil's surface

Previous studies which were issued in the journal had confirmed that if the sintering temperature was above 1000°C for 2 h, the TiO_2 can be completely reduced to Ti_4O_7 or Ti_5O_9 . This is a type of titanium suboxide which has the best chemical stability and electronic conductivity in the titanium oxide [13]. But in this research we found that the sintering temperature cannot be over 800°C . Because over 800°C titanium metal will react with titanium oxide fiercely and it will seriously affect the titanium plate strength so that it cannot act as the substrate material. Accordingly, the temperature affects titanium modified effect very obviously. Thus, in this paper we characterized the microstructure, micromorphology and electrical conductivity of the modified titanium foil's surface under different temperature.

The X-ray diffraction patterns for modified titanium surface under different temperature were presented in Fig 3. From Fig 3 it can be shown that compared to standard spectra of titanium dioxide (PDF#21-1276), the primary pattern of modified titanium surface corresponds to that of TiO_2 . It implied that after high temperature sintering the titanium foil surface was still mainly a layer of titanium dioxide. As can be observed in the diffraction peaks, with the increase of sintering temperature the intensity of the diffraction peak at two theta angle 27° reduced significantly. The change of the diffraction peak intensity means the crystal structure of titanium dioxide was altered. These kinds of changes include the change of grain structure and material composition in the crystal in according to the analysis principle of X-ray diffraction. Compare with the diffraction peaks between 30° and 50° of two theta angles, as the sintering temperature raised the number of diffraction peaks also increased. It means that when the sintering rose to 800°C , other substances presented in the modified titanium foil surface in addition to titanium dioxide. Compared with standard PDF cards (PDF#50-0788, PDF#50-0789, et al.) we can find that these substances should be some titanium dioxide losing a part of the oxygen atom. It suggested that titanium dioxide can be partially restored and lost a part of the oxygen atom with carbon in the high sintering temperature conditions in order to appear some oxygen vacancies in the titanium dioxide lattice. These oxygen vacancies can provide channels for the conduction of electrons. Thus, with the temperature rises, the amount of oxygen defects in titanium dioxide lattice increased and it would make the material has more superior electronic conductivity.

Fig 4 showed the micromorphology of modified titanium surface under the changed temperature. It suggested that at 600°C metal lattices were arranged very neatly. At 700°C , the metal lattice arrangement appeared slightly confused. However, when the sintering temperature reached 800°C , the confusion degree of the metal lattice increased obviously. In the SEM image orderly metal lattice arrangement was on the brink of nonexistent. This was primarily because that the existence of crystal defects damaged the titanium dioxide metal lattice arrangement and this made it become confusion. From Fig. 4, it also can be established that with the rising of temperature, the diameter grain size of a particle reduced in gradually. As is known to all, the grain size is smaller,

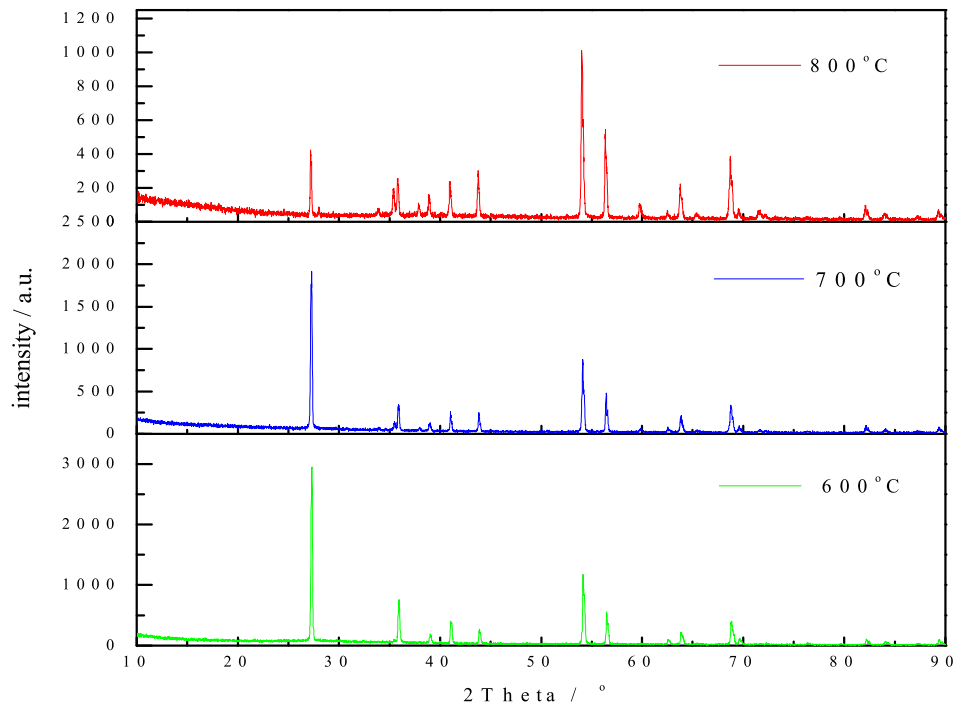


Fig. 3. X-ray diffraction patterns for modified titanium surface under different sintering temperature.

and the surface area of material is larger. Because the electronic conductivity of materials is inversely proportional to its surface area, when the temperature was 800 °C the surface of titanium foil should have the greatest superior electronic conductivity.

Through the electronic conductivity test, we learned that at 600 °C the electrical conductivity of modified titanium foil was quite poor. The resistance had been over the instrument's measuring range. However, when the sintering temperature raised

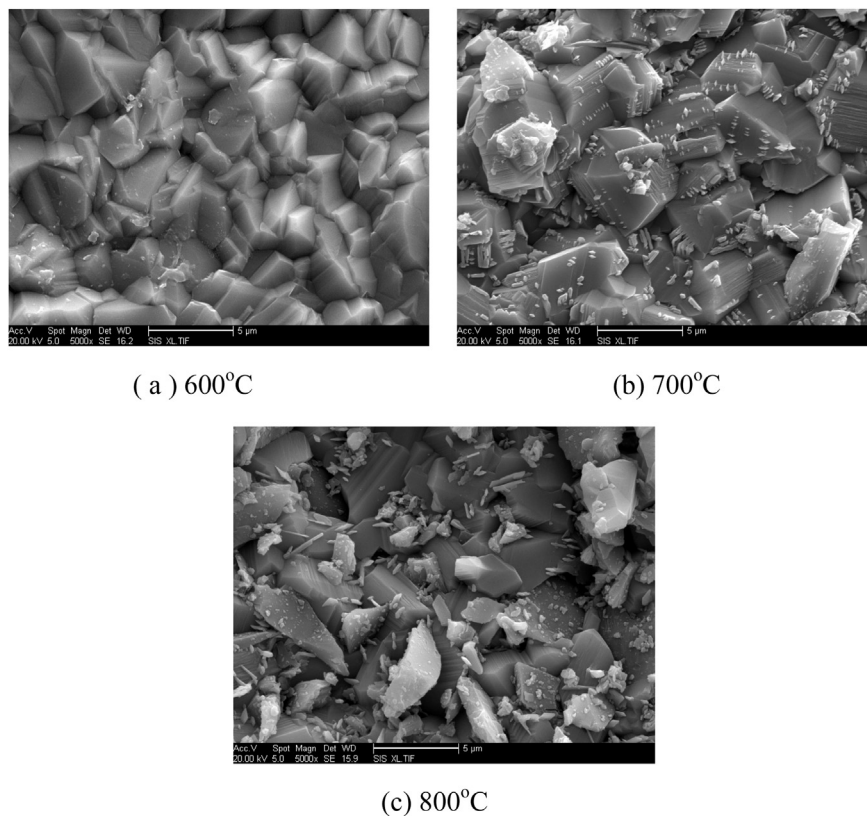


Fig. 4. SEM images of modified titanium surface under the different sintering temperature.

to 700 °C the electrical conductivity reached 10^{-5} – 10^{-4} S cm $^{-1}$. And when the temperature reaches 800 °C, the electrical conductivity reached 10^{-2} – 10^{-1} S cm $^{-1}$.

This seems to indicate that after sintering at 800 °C the electrical conductivity of modified titanium foil had been improved obviously. Although, saw from the results, after coating a layer of TiO $_{2-x}$ the electronic conductivity of titanium foil was still not very ideal compared to lead–tin alloy and barium metaplumbate (BaPbO $_3$), it also can meet the need of the substrate for bipolar lead-acid battery.

3.2. Electrochemical performance of the bipolar lead-acid battery

Titanium foil surface was coated with TiO $_{2-x}$ in order to prevent the titanium from oxidation due to the positive strong oxidizing and high electrode potential and in consequence of studying on the performance of positive active material of bipolar lead-acid battery.

Fig 5 showed voltages versus specific capacity charge–discharge profiles for the positive active material of bipolar lead-acid battery with Ti foils coated with TiO $_{2-x}$ as substrate at 0.5C rate. It was shown that the discharge potential was between 4.2 V and 4.4 V. The voltage between the charge and discharge voltage platform was only 0.3 V. The initial discharge specific capacity was 80 mAh g $^{-1}$. This suggested that in spite of the electronic conductivity of TiO $_{2-x}$ coated on the titanium surface was far lower than that of titanium metal, but it didn't seriously affect the charge–discharge properties of the positive active material of bipolar lead-acid battery.

Fig 6 showed voltages versus specific capacity discharge profiles for positive active material of bipolar lead acid battery with TiO $_{2-x}$ coated Ti foils as substrate at 0.5, 1C and 2C rate. From Fig. 6, it can be observed that with the increase of current density, the discharge potential platform was not decreased obviously. When the current densities were at 0.5C, 1C, 2C, discharge capacities respectively were 80 mAh g $^{-1}$, 70 mAh g $^{-1}$, and 60 mAh g $^{-1}$. From the discharge potential platform it showed that the potential platform was sufficiently plain, and when the current densities increased from 0.5C to 2C the potential platform reduced from 4.4 V to 4.3 V. This is mentioned that the increase of current density did not fall the discharge voltage platform significantly and the capacity was not obviously reduced. This was mainly due to the current transfer mode and the special structure (the existence of the substrate) of

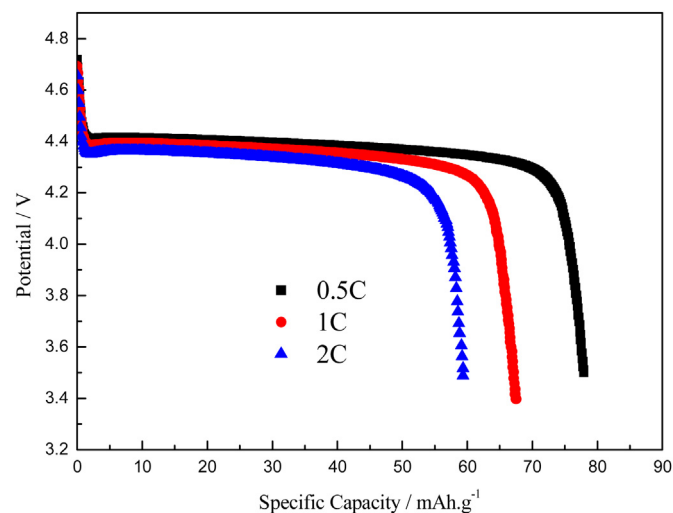


Fig. 6. Discharge characteristics of the positive active material of bipolar lead-acid battery with Ti plate coated with TiO $_{2-x}$ as substrate at 0.5C, 1C and 2C rate.

the bipolar lead-acid battery and that can make the ohmic resistance decrease and the current density also can evenly distribute.

Fig 7 showed the cycling performance of the discharge capacities of the positive material of bipolar lead-acid battery with pure titanium foils and modified titanium foils as substrate at 0.5C rate. It showed that the specific capacity of positive active material with pure titanium foil as substrate was slightly higher than the modified titanium foil in the initial 50 cycles. This was explained by the fact that at the beginning of charge/discharge cycle, the surface titanium foil didn't form a thick and intact TiO $_2$ layer. At this time, the electronic conductivity of pure titanium foil was better than modified titanium foil. Therefore, the specific capacity was slightly higher. However, after 60 cycles the specific capacity with pure titanium foils as substrate started to decrease rapidly. After 90 cycles, the specific capacity with pure titanium foils as substrate only had 60 mAh g $^{-1}$ while after 100 cycles, the discharge capacity still maintained at 70 mAh g $^{-1}$. Compared to the initial discharge capacity, using pure titanium foils as substrate the specific capacity decreased more than 25% while using modified foils as substrate it only decreased 12.5%. This implies that coated with a layer of TiO $_{2-x}$

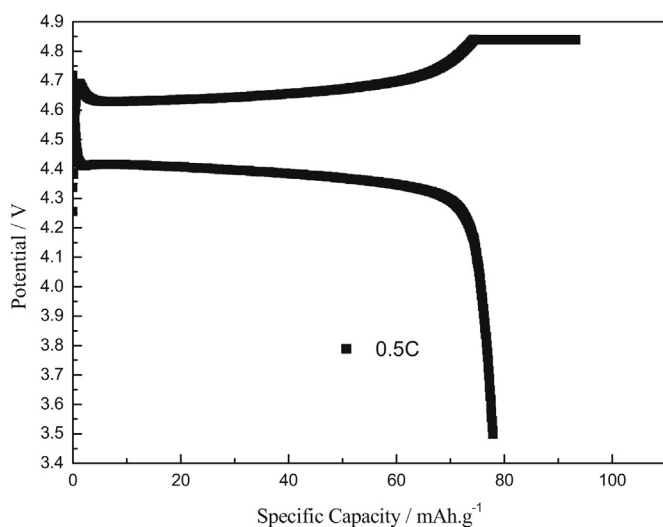


Fig. 5. Charge–discharge curves of the positive active material of bipolar lead-acid battery with Ti plate coated with TiO $_{2-x}$ as substrate at 0.5C rate.

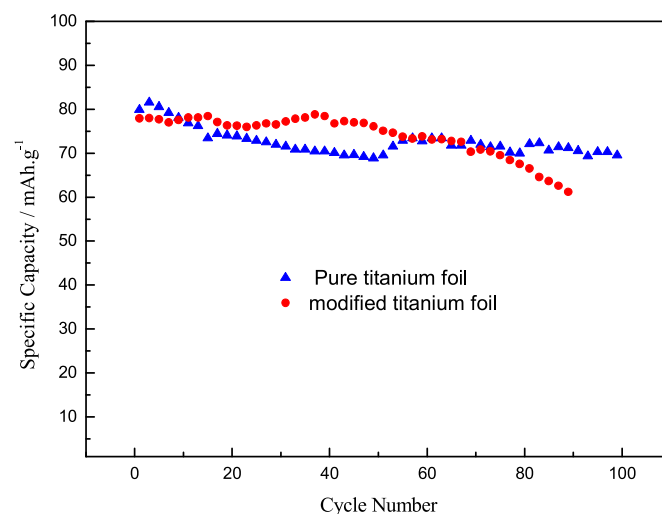


Fig. 7. Cycle performance of the positive active material of bipolar lead-acid battery with pure titanium foil and modified titanium foil as substrate at 0.5C rate.

on the titanium's surface can effectively improve the chemical stability of titanium foil in the high potential and strong oxidizing conditions. In the process of charge and discharge, the properties of substrate for bipolar lead-acid battery can maintain stability.

Above all, modifying titanium foils with coating a lay of TiO_{2-x} on the surface can be a kind of ideal material as the substrate for bipolar lead-acid battery in terms of its electrochemical performances.

4. Conclusions

The paper mainly studied titanium foil coated with TiO_{2-x} by means of sol–gel method as the substrate material for bipolar lead-acid battery. Through the XRD, SEM and four-probe test, the microstructure, micromorphology, material composition and electronic conductivity of modified titanium foil's surface were characterized. Compared with different sintering temperature, we found that the modified titanium surface has the highest electronic conductivity and the most superior microstructure and morphology under the sintering temperature of 800 °C.

Through the study on the performance of positive active material of bipolar lead-acid battery with Ti coated TiO_{2-x} as substrate, the results showed that when charged and discharged in 3.5 V–4.84 V with the rate of 0.5C, the voltage between the charge and discharge voltage platform was only 0.3 V, and the initial discharge specific capacity can achieve 80 mAh g⁻¹. When the current rate was up to 1C and 2C, the initial discharge specific capacity was 70 mAh g⁻¹ and 60 mAh g⁻¹. It suggested that in spite of the titanium surface coated with a lay of TiO_{2-x} , but it didn't affect the charge–discharge properties of the positive active material of bipolar lead-acid battery.

Compared with using pure titanium foil as substrate for bipolar lead-acid battery, the specific capacity with modified titanium foils as substrate was only decreased 12.5% of the initial capacity after 100 cycles while using pure titanium foils as bipolar it had decreased 25% after 90 cycles. It was of the view that coated with a

layer of TiO_{2-x} on the titanium's surface can effectively improve the chemical stability of titanium foil in the high potential and strong oxidizing conditions. In the process of charge and discharge, the properties of substrate for bipolar lead-acid battery can maintain stability.

Through the above research, we can know that Ti coated with TiO_{2-x} by means of sol–gel method can be a type of ideal material as the substrate for bipolar lead-acid battery.

Acknowledgments

The authors thank Huafu Company in Jiangsu province in China for providing financial assistance and the various manufactured components used in this research.

References

- [1] D. Linden, T.B. Reddy, *Handbook of Batteries*, McGraw-Hill, New York, 1993.
- [2] Joern Albers, Eberhard Meissner, Sepehr Shirazi, *J. Power Sources* 196 (2011) 3993–4002.
- [3] M. Saakes, R. Woortmeijer, D. Schmal, *J. Power Sources* 144 (2005) 536–545.
- [4] H. Karami, M. Shamsipur, S. Ghasemi, M.G. Mousavi, *J. Power Sources* 164 (2007) 896–904.
- [5] I. Paleska, R. Pruszkowska-Drachal, J. kotowski, et al., *J. Power Sources* 129 (2004) 326–329.
- [6] Keith Ellis, Andrew Hill, John Hill, et al., *J. Power Sources* 136 (2004) 366–371.
- [7] Xiaoxia Li, Aaron Li Zhu, Wei Qu, et al., *Electrochim. Acta* 55 (2010) 5891–5898.
- [8] Tomoki Tsumura, Yoshiyuki Hattori, Katsumi Kaneko, et al., *Desalination* 169 (2004) 269–275.
- [9] Young-Chul Woo, Ho-Jae Kang, Deug J. Kim, *J. Eur. Ceram. Soc.* 27 (2007) 719–722.
- [10] Chao Tang, Debi Zhou, Qing Zhang, *Mater. Lett.* 79 (2012) 42–44.
- [11] Fu-Der Mai, Wen-Lian William Lee, Jia-Lin Chang, et al., *J. Hazard. Mater.* 177 (2010) 864–875.
- [12] Lei Hana, Yanjun Xina, Huiling Liu, et al., *J. Hazard. Mater.* 175 (2010) 524–531.
- [13] Jiaqing Li, Lei Zheng, Luoping Li, et al., *J. Hazard. Mater.* 139 (2007) 72–78.
- [14] Shaogui Yang, Yazi Liu, Cheng Sun, *Appl. Catal. A Gen.* 301 (2006) 284–291.
- [15] Yunlan Xu, Yi He, Xinde Cao, et al., *Environ. Sci. Technol.* 42 (2008) 2612–2617.